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Self-Energy corrections to DFT-LDA Gaps of Realistic Carbon Nanotubes

Guido Satta, Giancarlo Cappellini, and Francesco Casula
INFM and Dipartimento di Fisica, Università di Cagliari, I-09042 Cagliari, Italy

ABSTRACT

Since their discovery carbon nanotubes have attracted much interest for their peculiar electronic properties which go from metallic to semiconducting behaviour, depending both on diameter and chirality. The exact value of their band gap is obviously a crucial point to be addressed because it enters in the nanotube application as microelectronic devices. By making use of an efficient GW scheme, previously tested on bulk systems, as well as of a model screening function, we obtaind for the first time excitation energies and band-gap values for carbon nanotubes. Results for $(6,0)$ and $(7,0)$ will be presented and discussed.

Introduction

Since their discovery [1] in 1991 carbon nanotubes have attracted much attention for their peculiar mechanical and electronic properties. As it is well known, their structure can be thought as obtained by rolling up a graphite sheet in such a way that the carbon atoms along a given direction are arranged in parallel rings orthogonal to the tube axis. If after the wrapping procedure a lattice site of a graphite sheet turns out to coincide with the site originally displaced by a vector

$$\mathbf{c} = n\mathbf{a_1} + m\mathbf{a_2}, \tag{1}$$

$\mathbf{a_1} = (a\sqrt{3}, 0)$ and $\mathbf{a_2} = (a\sqrt{3}/2, 3a/2)$ being the graphite lattice vectors, the nanotube is uniquely identified by the indices (n,m). Actually both the tube diameter d and the chiral angle, i.e. the angle between $\mathbf{c}$ and $\mathbf{a}_1$, can be easily expressed in terms of n and m:

$$d = \frac{\sqrt{3}\sqrt{n^2 + m^2 + nm}}{\pi} a, \tag{2}$$

$$d = \ tg\theta = \frac{\sqrt{3}m}{2n + m}, \tag{3}$$

$a = 1.42\mathring{A}$ being the nearest neighbor distance of carbon atoms in graphite. For obvious geometrical reasons chiral angles range between $\theta = 0$ and $\theta = \pi/6$, where the two limiting cases are strictly speaking not chiral ones. The $\theta = 0$ and $\theta = \pi/6$ wrappings correspond to (n,0) and (n,n) indices and are popularly known as zig-zag nanotubes and armchair nanotubes respectively.

Carbon nanotubes diameters range in the nanometer size, whilst their lenght is in the millimiter size, and small changes in helicity and diameter can shift their electronic character from insulating to semiconducting and to metallic. Moreover spontaneous or induced mechanical distortions can dramatically affect their properties. If one now takes into account the possibility of growing multiwalled nanotubes, i.e. co-axial carbon tubes, or of arranging them in bundles, one can easily understand how many different physical properties can be obtained by modifying the same basic object. Obviously these systems have

been submitted to theoretical investigation, in order to reproduce the experimental results and to predict specific material properties. [2, 5]

We have reported in a previous paper [6] the results of our calculations on several armchair and zig-zag single-wall finite nanotubes, performed by the discrete variational method (DVM) within DFT-LDA approximation. We refer to the original paper, as well as to other DVM-based papers for discussing the reliability of such computational approach [7, 8, 9]. In principle our results should be of comparable quality with any LDA results for similar systems. Actually we can use them also for estimating the electronic properties of infinite nanotubes, provided that the border effects in the local densities of states go rapidly to zero, as soon as states localized on the inner carbon rings are considered. In this way we have been able to obtain predictions for the gaps of quite large carbon nanotubes in reasonable agreement with previous LDA results, if any, and with a very reasonable computational effort.

Still remains the problem of a direct determination of the LDA gaps in infinite carbon nanotubes as well as the problem of correctly estimating their excitation properties. In fact, DFT-LDA approximation has been successfully used for determining the ground-state electronic properties of a large class of materials ranging from bulk systems, surfaces and etherostructures to atoms and clusters. [10] On the other hand if DFT-LDA is used to determine the quasiparticle (QP) spectra of many-electron systems in most cases results are in disagreement with experiments.[10] For example, in the case of bulk semiconductors, assumption of the Kohn-Sham (K-S) eigenvalues as electronic QP energies leads to a systematic underestimate of the electronic transition energies with respect to the experiment (*band-gap problem*). [11, 12, 13]

QP properties of many-electron systems are correctly evaluated starting from the QP equations, in which the full electronic self-energy operator appears. [14] The self-energy operator is treated usually in the GW approximation (GWA) by starting from DFT-LDA eigenvalues and eigenfunctions used to evaluate the one-electron Green function and the screened Coulomb interaction.[11, 12] Until now the numerical effort required to calculate the dynamical screened interaction (W) for the GW self-energy has restricted the systematic solution of the QP problem mainly to simple structures. [15] In this work for the first time GW self-energy corrections for the (6,0) and (7,0) nanotubes have been calculated. The present results demonstrate the possibility to apply our method to larger graphene systems.

Computational Method

Ab initio calculations of the electronic properties of infinite isolated carbon nanotubes have been performed by using a plane wave basis set and ionic pseudopotentials for Carbon after Troullier and Martins [16]. Angular components of ionic pseudopotentials up to $l = 2$ have been included . In particular we have considered the case of zig-zag nanotubes with indeces (6,0) and (7,0). A repeated-cell approach has been used, and in order to correctly simulate the isolated structures of nanotubes, distances in the directions orthogonal to the nanotube axis have been accurately chosen. Moreover we have performed two different kinds of convergence tests, i.e. with respect to energy cutoff and to dimensions of the simulation cell. In the case of the (6,0) structure a $3a$x$12a$x$12a$ cell with 24-atom basis has been used. (see figure 1)

While $3a = 8$ *a.u.* is the length of the unitary structure to be repeated along the graphene

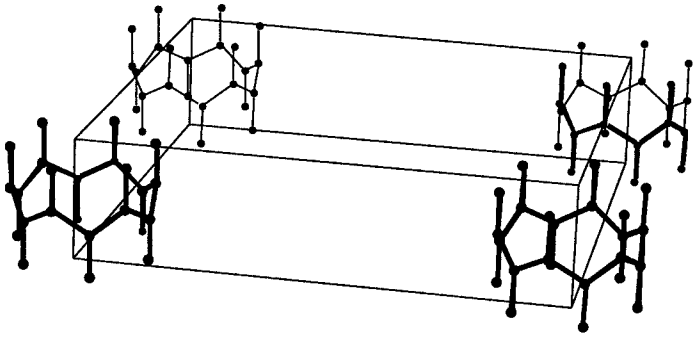

Figure 1: simulation cell for (6,0) structure

nanotube, the $32a.u.$ sides garantee a sufficiently large distance between atoms belonging to different nanotubes (as a term of comparison the interplanar distance in graphite is $d = 6.34\ a.u.$.).

Within our simulation cell the minimal distance between carbon atoms belonging to different nanotubes turns out to be greater than 23 a.u. For what attains to the energy cutoff, values up to 30 Ry have been considered. In sampling the first BZ for calculating the nanotube charge density only the Γ point has been used. This choice has been obviously dictated by the need of drastically reducing the computational effort in such a large unit cell. On the other hand the BZ of the system is correspondingly small, which should justify our choice, as we shall see later on in the discussion of the results. The same technicalities have been used in calculating LDA energies of $(7,0)$ nanotube.

An efficient DFT-GW method has been used to determine the quasiparticle correction of the band-gap of (6,0) and (7,0) nanotubes. It has been originally developed for the calculation of quasiparticle energies of cubic semiconductors [17] and then succesfully extended to systems of lower symmetry such as SiC polytypes [18] and oxides [19]. Local fields effects in the screening of the material are described within an LDA-like approximation, and dynamical effects are treated by expanding the self-energy operator to linear order in energy. The anisotropy of the inverse dielectric matrix is taken into account simply averaging over three directions:

$$\frac{1}{\epsilon_\infty} = \frac{a}{\epsilon_{||}} + \frac{b}{\epsilon_\perp} \tag{4}$$

a and b being two weighting factors which take into account the different screening properties along the tube and in the orthogonal directions. If we imagine to start from the structure of the graphitic plane we have that $\epsilon_{||}$ is the in plane component and $\epsilon_\perp$ is the component perpendicular to the plane. This simple approximation permits us the use of a cubic cell to perform self-energy calculations with a strong reduction of computational effort. In

Table I: Band gap energies for $(6,0)$ and $(7,0)$ zig-zag nanotubes calculated with DVM approch (first column) DFT-LDA approach (second column). In the third column previous DFT-LDA results after Ref.[20]

(n,m)	DVM	LDA(pw)	LDA(Ref.[20])
$(6,0)$	0.0	$Metal(-0.74)$	$Metal(-0.83)$
$(7,0)$	1.04	0.18	0.09

Table II: GW quasi-particle corrections to band gap energies for $(6,0)$ and $(7,0)$ zig-zag nanotubes calculated with different ϵ_∞ values (see text).The energies are in eV

ϵ_∞	$(6,0)$	$(7,0)$
240	0.04	
7.06	0.41	0.651

order to keep a sufficiently large distance between atoms of different isolated nanotubes the cube side must be at least twice as large as the minimal $3a$ one, so that 8 carbon rings are included along the cell vertical axis. In this way the minimal distance between atoms belonging to different (6,0) nanotubes turns out to be at least 1.14 times the minimal distance between atoms belonging to different planes in graphite. In (7,0) nanotubes the corresponding distance is 0.91 times that of graphite. The results for the gap values will confirm this assumption. The self-energy correction of the eigenvalue $E^0_{n\mathbf{k}}$ relative to the Bloch state $|n\mathbf{k}>$ is calculated according to equation [17]

$$\Delta_{n\mathbf{k}} = E_{n\mathbf{k}} - E^0_{n\mathbf{k}} = \frac{[\Sigma^{COH}_{n\mathbf{k}} + \Sigma^{SEX}_{n\mathbf{k}} + \Sigma^{DYN}_{n\mathbf{k}}(E^0) - V^{XC}_{n\mathbf{k}}]}{1+\beta_{n\mathbf{k}}}, \tag{5}$$

where the terms appearing in the third member of the equation are the static Coulomb Hole (COH) and Screened Exchange terms (SEX), the expectation value of the DFT-LDA exchange-correlation potential,and of the two dynamical terms Σ^{DYN} and β (see Refs. [17] and [18]). The singularity of the Coulomb potential in the screened-exchange part of the electronic self-energy is treated by using auxiliary functions of the appropriate symmetry [18].

Results and Discussion

In Tab. I we have shown the results of our LDA calculation for the $(6,0)$ and $(7,0)$ nanotubes compared with previous results. We note the our result for the gap of the $(7,0)$ structure is slightly different from the result of Ref. [20]. This difference can be reasonably explained by taking into account the different cutoff, and the different relaxation of the structure.

In any case our calculations reproduce the same trend previously reported in ref. [20], with semiconduting properties for the $(7,0)$ structure and metallic properties for the $(6,0)$ one. The band structure and the energy-level ordering results in good agreement too.

In Tab. II we have reported the GW corrections to the band gap values obtained with our method for the (6,0) and (7,0) zig-zag nanotubes. The corrections are calculated with ϵ_∞ obtained from equation (4) . The two components are estimated from graphite parameter, in particular we follow ref. [21] and we put the value $\epsilon_\perp = 2.4$ and for $\epsilon_{||}$ we use a value 100 times greater [21]. With $a = 1$ and $b = 0$, i.e. complete metallic screening, for the $(6,0)$ a very small GW correction results. On the other hand even with a more semiconducting behaviour $\epsilon_\infty = 7.06$, obtained with $a = 2/3$ and $b = 1/3$ in equation 4 the structure maintains a metallic character. For the $(7,0)$ nanotube we confirm including GW corrections the DFT-LDA prediction of a semiconducting behaviour, with a enhancement of the gap due to self-energy corrections.

To summarize, we have presented in this paper DFT- LDA calculations with GW corrections for the band-gap of $(6,0)$ and $(7,0)$ carbon nanotubes. Our DFT-LDA results have been compared with previous theoretical ones in order to prove the accuracy of the present computational method. For $(6,0)$ nanotube our LDA results are in good agreement with previous similar calculations and our GW corrections confirm the metallic character of this tube. On the other hand $(7,0)$ nanotubes appears to be semiconductors with a relevant GW gap correction. Since C nanotubes as small as $3,3)$ ones have been detected [22, 23], one can expect that specific measurements even for small nanotubes can be available in the next future, thus eventually confirming our predictions. Moreover the combination of different approaches, say cluster calculations, repeated cell ones and GW corrections, depending on the properties one is looking for, turn to be very useful in addressing such kind of systems.

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